Small angle neutron scattering studies of a polybutadiene/polystyrene blend with small additions of ortho-dichloro-benzene for varying temperatures and pressures. II. Phase boundaries and Flory–Huggins parameter

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Two polymer blends of polybutadiene and polystyrene are investigated by small angle neutron scattering as a function of pressure and solvent content. We measured the thermal composition fluctuations, which we described with crossover functions. Whereas the crossover behavior of the susceptibility and the correlation length was the subject of Paper I [J. Chem. Phys. **116**, 2229 (2002)], here we discuss the phase boundaries and the extracted mean-field effective Flory–Huggins parameter and radius of gyration for the asymptotic behavior at high temperatures. Using a lattice model and the lattice cluster theory of Bawendi and Freed, we developed some general expressions for the dependence of the Flory–Huggins parameter on the excess free volume and on the solvent content. A compensation of the free volume by the solvent molecules was observed. Finally, a discussion of the Clausius–Clapeyron equation allows for a check of the crossover function used to extract mean-field quantities for comparison with theory. © *2002 American Institute of Physics*. [DOI: 10.1063/1.1429960]

I. INTRODUCTION

This paper deals with experiment data and their analysis for thermal composition fluctuations, which are always present in multicomponent systems. The fluctuations in one-phase regions are usually weak at high temperatures and become strong close to the critical point. Two universal behaviors are found, corresponding to temperatures far above and near to the critical point. Mean-field behavior is associated with the presence of weak fluctuations, which occur at high temperatures far from the critical point.

The first mean-field model for polymer blends was Flory–Huggins theory,[1] which describes the Gibbs free energy of mixing as the sum of a combinatorial entropy and an interaction term, characterized by the effective Flory–Huggins interaction parameter Γ. Experiments found that Γ has both enthalpic and entropic contributions. Theoretical extensions of the Flory–Huggins model followed in order to explain the presence of the unexpected noncombinatorial entropic contributions, and these extensions elaborated further details of the enthalpic portion. The additional entropy is connected with several features omitted from the original Flory–Huggins theory, including system compressibility,[2–4] monomer structures and nonrandom mixing,[3,5–7] chain stiffness,[8–10] and chain end effects.[9,11] In principle, the enthalpy is influenced by all these effects as well. In parallel, qualitative arguments were used by Flory[12] to describe contributions from the presence of excess free volume, which provides a similar understanding of compressibility effects. The more refined theories describe the local correlations (or nonrandom mixing) on length scales of basically a monomer size. These microscopic models produce extended mean-field descriptions of multicomponent polymer systems.

The other universal behavior for polymer blends is 3D-Ising behavior that emerges close enough to the critical point. The 3D-Ising critical amplitudes for approaches to the critical point from above and below the critical temperature are connected,[13] but a more microscopic understanding of the 3D-Ising behavior is still lacking. Experiments measuring the pressure dependence showed that neither pressure nor microstructure exerts a major influence on the critical amplitudes.[5] This result is consistent with scaling arguments that predict a universal dependence of the critical properties on the degree of polymerization.[14]

Here, we describe further systematic studies and analyses of SANS experiments for several ternary mixtures consisting of a symmetrical polymer blend (same molecular weights and volume fractions) and different amounts of a nonselective solvent. The experimental details are presented in the preceding paper;[15] hereby referred to as Part I. In the present paper we discuss the phase boundaries and mean-field quantities, which were evaluated from the crossover behavior of the susceptibility $S(0)$ and the correlation length ξ, as given by the high temperature asymptotic behavior, $S(0)=C_+^{\mathrm{MF}}\tau^{-\gamma}$ and $\xi=\xi_0^{\mathrm{MF}}\tau^{-\nu}$, with C_+^{MF} and ξ_0^{MF} being the mean-field critical amplitudes, $\tau=|T-T_C|/T$ being the reduced temperature with respect to the critical temperature T_C, and $\gamma=1$ and $\nu=0.5$ being the mean-field critical exponents. In order to extract the asymptotic mean-field behav-

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ior from the experimental data, a crossover function is required since we typically perform measurements in the 3D-Ising and the crossover ranges. The mean-field quantities extracted in this fashion are parameters that are free of contributions from long-range composition fluctuations.

The measured mean-field quantities are explained by extending the original work of Bawendi and Freed[16] one step further, i.e., we extend their lattice model to a three-component system consisting of two polymers plus a nonselective solvent. While subsequent elaboration of the lattice cluster theory includes a description of monomer molecular structure,[3,7] here we apply this simpler treatment that assigns individual monomers to single lattice sites because of our desire both to extract the basic physics and to greatly simplify the algebra. This model suffices to provide a general description for the influence of the free volume and the solvent on the phase behavior of these ternary systems. While the theory qualitatively describes the experimental dependence, the observed variation proves to be much stronger than theoretically estimated, presumably, in part, due to the simplifications in using a single lattice site to house individual monomers, i.e., due to ignoring monomer structure and the nontrivial chain-end effects arising from using polymers with low molar volumes and with chemically distinct end groups.[8]

II. THEORETICAL BACKGROUND

In this section we discuss the theoretical description of the mean-field quantities. We therefore use the lattice cluster theory developed by Bawendi and Freed.[16] Furthermore, we briefly explain how the mean-field quantities are obtained from the crossover functions.

A. The Flory–Huggins parameter

The mean-field properties of a polymer blend are represented in terms of the effective Flory–Huggins parameter Γ. Our previous paper[15] described how to obtain this mean-field parameter from measurements that are influenced by strong fluctuations. Experiments and theory found that the Flory–Huggins parameter has both an entropic and an enthalpic portion Γ_σ and Γ_h

$$\Gamma = \Gamma_h / T - \Gamma_\sigma . \tag{1}$$

Whereas the enthalpic portion emerges from energetic interactions, the entropic portion arises from many contributions. Widely discussed entropic contributions are from the presence of excess free volume,[2,3] monomer structure,[3,5–7] chain flexibility,[8] and chain-end effects.[11,17] The present paper also includes the presence of the diluent solvent as a source of additional entropy in Γ. The single-site monomer version of the lattice cluster theory is used for a qualitative description to elucidate the physical origins of these contributions.

Technically, we obtain the critical mean-field amplitude C_+^{MF} from the experimental susceptibility, which is described by a crossover function and which is obtained experimentally from the extrapolated zero angle neutron scattering intensity. The critical mean-field amplitude is related to the entropic and enthalpic portions of the Flory–Huggins parameter via[15]

$$C_+^{\mathrm{MF}} = \tfrac{1}{2} / |\Gamma_C + \Phi_P \Gamma_\sigma| = \tfrac{1}{2} T_C^{\mathrm{MF}} / (\Phi_P \Gamma_h). \tag{2}$$

The reciprocal of the mean-field critical amplitude C_+^{MF} provides the entire entropic portion, written as $\Gamma_C + \Phi_P \Gamma_\sigma$, with Φ_P being the polymer content. [The dilution approximation will be discussed with Eqs. (9) and (10).] Γ_C is the Flory–Huggins parameter at the critical point. Another interpretation of the inverse of C_+^{MF} is given by the enthalpic portion Γ_h divided by the mean-field critical temperature.

B. Lattice cluster theory

In general, all thermodynamic properties of a system can be derived from its thermodynamic potential. The lattice model[16] uses N_L lattice sites, on which n_i polymer chains are placed. The N_i monomers per chain occupy the lattice sites (for species $i = \mathrm{A}, \mathrm{B}$). The n_s solvent molecules each occupy the same single lattice site. Vacant lattice sites simulate the presence of free volume (voids) and therefore model the compressibility of the system. (Note that the voids are not actual components in the thermodynamic sense.) The use of a common volume for all monomers of both species, solvent molecules, and voids is, of course, a gross simplification applied here to extract a leading general understanding of the basic physical phenomena and to simplify the algebra greatly.

The Helmholtz free energy of mixing ΔF of a ternary polymer–polymer–solvent–void system, normalized by the sample volume V_{Samp} and the thermal energy $k_B T$, is written generally in the form

$$\begin{aligned} \frac{\Delta F}{V_{\mathrm{Samp}} k_B T} = & \frac{\phi_A \ln \phi_A}{V_A} + \frac{\phi_B \ln \phi_B}{V_B} + \frac{\phi_S \ln \phi_S}{V_S} \\ & + \frac{\phi_V \ln \phi_V}{V_{\mathrm{cell}}} + g_{AB}\phi_A\phi_B + g_{AS}\phi_A\phi_S \\ & + g_{AV}\phi_A\phi_V + g_{BS}\phi_B\phi_S + g_{BV}\phi_B\phi_V \\ & + g_{SV}\phi_S\phi_V . \end{aligned} \tag{3}$$

The first terms represent the combinatorial entropy of the A and B polymers, the solvent, and the translational entropy, which is conveniently written in terms of the excess free volume, respectively, with the corresponding site fractions ϕ_A, ϕ_B, ϕ_S, ϕ_V, and the corresponding molar volumes V_A, V_B, V_S, $\mathrm{V}_{\mathrm{cell}}$. Note that the free-volume fraction $\phi_V = 1 - \phi_A - \phi_B - \phi_S$ is not an independent variable. The last terms involve generalized interaction parameters g_{ij} between the different components. We follow the lattice cluster theory calculations of Bawendi and Freed[16] and discuss details in Appendix B.

The potential F is used to determine the partial structure factors from the chemical potentials μ_i following Ref. 18. The change from $\{\partial n / \partial \mu\}$ to $\{\partial \mu / \partial n\}$ is accomplished by matrix inversion

$$S_{ij}(0) = V_i V_j k_B T \left\{ \frac{\partial \mu}{\partial n} \right\}_{ij}^{-1}$$

$$\text{with } \mu_i = \left.\frac{\partial F}{\partial n_i}\right|_{T,V,n_{j\neq i}} \quad \text{and } i = A,B,S. \tag{4}$$

The partial structure factors are then used to calculate the scattering cross section through

$$\frac{d\Sigma}{d\Omega}(0) = \frac{1}{V_{\text{Samp}}}(\rho_A^2 S_{AA} + \rho_B^2 S_{BB} + \rho_S^2 S_{SS} + \rho_A\rho_B S_{AB} + \rho_A\rho_S S_{AS} + \rho_B\rho_S S_{BS}). \tag{5}$$

By using the relative scattering length densities ρ_i with the solvent as a standard, we arrive at Eq. (2) of Ref. 15. This expression is based on ignoring contributions from total density fluctuations. As a further step [Eq. (3) of Ref. 15], the scattering cross section can be split into one portion describing the composition fluctuations and another describing the overall polymer density fluctuations. This simplification assumes symmetry between the two polymers

$$\frac{d\Sigma}{d\Omega}(0) = K_{AB}\Phi_P S(0) + K_{PS} S_{PP}(0). \tag{6}$$

The scattering contrasts are defined as $K_{AB} = (\rho_A - \rho_B)^2/N_A$ and $K_{PS} = (\bar{\rho} - \rho_S)^2/N_A$. Based on the actual magnitudes of the scattering length densities ρ_i, we argued that the composition fluctuation term is dominant here. An equivalent representation of required susceptibility $S(0)$ is obtained by directly projecting the composition fluctuation contributions from the matrix $\{S_{ij}\}$

$$\frac{1}{K_{AB}}\frac{d\Sigma}{d\Omega}(0) = \Phi_P S(0) = \frac{1}{V_{\text{Samp}}}\frac{1}{4}(S_{AA} + S_{BB} - 2S_{AB}). \tag{7}$$

A comparison with classic Flory–Huggins theory requires the reciprocal susceptibility, which is a projection of the inverse matrix of $\{\partial\mu/\partial n\}$. We developed an approximation given in Appendix A which results in the form

$$\frac{K_{AB}}{d\Sigma/d\Omega(0)} = \frac{1}{\Phi_P S(0)} = \frac{1}{V_{\text{Samp}} k_B T}\left(\frac{\partial^2 F}{\partial\phi_A^2} + \frac{\partial^2 F}{\partial\phi_B^2} - 2\frac{\partial^2 F}{\partial\phi_A\partial\phi_B}\right). \tag{8}$$

This representation involves a change of variables such that the differentiation is with respect to the volume fractions ϕ_i (instead of the particle numbers n_i). Therefore, the factors of V_i cancel out. Again, note that the free-volume fraction $\phi_V = 1 - \phi_A - \phi_B - \phi_S$ is not an independent variable.

The reciprocal susceptibility is then used to define the effective interaction parameter Γ

$$\frac{K_{AB}}{d\Sigma/d\Omega(0)} = \frac{1}{\Phi_P S(0)} = \frac{1}{V_A\phi_A} + \frac{1}{V_B\phi_B} - 2\Gamma. \tag{9}$$

Thus, the reciprocal of the susceptibility is given by terms arising from the combinatorial entropy of the two polymers plus an effective interaction parameter Γ. Equation (9), together with Eq. (8), represents the definition of the Flory–Huggins parameter Γ. The Flory–Huggins parameter contains a portion due to the interactions between the different particles that are described by the thermodynamic potential [Eq. (3)]. Equation (8) involves the polymer lattice concentrations ϕ_A and ϕ_B, which are not available experimentally. The dilution approximation[19] introduces the nominal concentrations $\Phi_A = \phi_A/\Phi_P$ and $\Phi_B = \phi_B/\Phi_P$ with $\Phi_P = \phi_A + \phi_B$, producing

$$\frac{1}{S(0)} = \frac{1}{V_A\Phi_A} + \frac{1}{V_B\Phi_B} - 2\Phi_P\Gamma. \tag{10}$$

The entropic portion of the Flory–Huggins parameter depends on both the solvent content and the amount of excess free volume. Using the lattice model we show (in Appendix B) that the leading contribution to Γ in the volume fractions of the excess free volume and solvent is of the form $\alpha(\phi_V + \phi_S)$, with α being a coefficient. A similar influence of excess free volume and solvent also emerges for nonsymmetric polymer systems [Eq. (A4)], where the leading contributions yield the following form for the entropic portion of the Flory–Huggins parameter:

$$\Gamma_\sigma = \Gamma_\sigma^0 + \frac{\phi_S}{\Omega_S} + \frac{\phi_V}{\Omega_V}. \tag{11}$$

Equation (11) adds a term Γ_σ^0 due to the neglected contributions to the entropic part of Γ_σ that arises from monomer structure, chain semiflexibility, and chain-end effects. The two additional terms in Eq. (11) describe the contributions due to the solvent and the excess free volume that are the focus of our investigation. The parameters Ω_S and Ω_V have the units of volume. Our comparisons with experiment show that this volume is of the order of the monomer, solvent, or void volumes. Within our current picture we find it plausible that $\Omega_S \approx \Omega_V$, since all calculations (Appendices A and B) found a common prefactor $\alpha = 1/\Omega_S = 1/\Omega_V$ (probably because the same lattice site is used for solvent molecules and for voids).

C. Radius of gyration

The radius of gyration is extracted from the high-temperature behavior of the correlation length. This procedure therefore first requires the extraction of the Flory–Huggins parameter from the high-temperature behavior of the susceptibility,

$$\xi_0^{\text{MF}} = R_g/\sqrt{3(1 + \Phi_P\Gamma_\sigma/\Gamma_C)}. \tag{12}$$

We stress that the evaluation of the radius of gyration also depends on the entropic portion of the Flory–Huggins parameter. This dependence on the entropic portion could induce a 100% error in the radius of gyration over that obtained from treatments in which the entropic portion is neglected. Furthermore, this radius of gyration is an average value of PB and PS.

D. Clausius–Clapeyron equation

We have discussed the classical Clausius–Clapeyron equation in a previous publication,[5] which reads

$$\frac{\Delta T_C}{\Delta P} = \frac{T_C V_m}{H_m}, \tag{13}$$

and which describes the pressure dependence of the phase transition temperature in terms of the differences of volume

V_m and enthalpy H_m between the two phases. Both these quantities can be related to Gibbs free energy of mixing and, therefore, to the Flory–Huggins free energy parameter χ. The observed SANS Flory–Huggins parameter Γ is related to χ via $\Gamma = \partial^2(\phi(1-\phi)\chi)/\partial\phi^2$. The Clausius–Clapeyron equation for polymer blends can then be expressed as

$$\frac{\partial T_C}{\partial P} = \frac{\partial \Gamma_h/\partial P - T_c \partial \Gamma_\sigma/\partial P}{\Gamma_h/T_C} - \frac{T_C}{1-Gi}\frac{\partial Gi}{\partial P}. \tag{14}$$

The first term on the right-hand side of Eq. (14) is the mean-field contribution that depends only on the Flory–Huggins parameter. The second term describes the influence of critical thermal fluctuations on the pressure dependence of the phase boundary. The latter term is based on the relation between the mean-field critical temperature T_C^{MF} and the actual critical temperature T_C, which reads $T_C = T_C^{\mathrm{MF}}/(1-\mathrm{Gi})$. For polymer blends, it is commonly found[20,5] that the Ginzburg number Gi decreases with pressure, which leads to a positive contribution to the pressure dependence of the phase boundary. For the d-PB(1,2)/PS system,[5] we found that the pressure dependence of the Ginzburg number can provide the dominant contribution.

III. RESULTS

The experimental setup for the SANS experiments is described in the preceding paper. All results emerge from measurements of the susceptibility and correlation length and the use of the crossover function.

A. Phase diagrams

The spinodal temperature is plotted as a function of the solvent content in Fig. 1(a). For either d-PB(1,4)/PS or d-PB(1,2;1,4)/PS blend, the spinodal temperature decreases with increasing solvent content. At a solvent content of 20%, an overall decrease in the spinodal temperatures is found to be 46 and 62 K, respectively, from the solvent-free blends. Hence, the diluent increases the miscibility and therefore acts as a mediator between the relatively immiscible polymers.

The pressure-dependent phase diagrams show a linear increase of the spinodal and binodal temperatures [Figs. 1(b), 1(c)] for different solvent contents and for the two different blends. Whereas the binodal for the d-PB(1,4)/PS blend was practically indistinguishable for higher solvent contents, the binodal of the d-PB(1,2;1,4)/PS blends was always observable as distinct from the spinodal. The separation between the binodal and spinodal is pressure independent. Again, the decrease of the spinodal with increasing solvent content is quite visible.

B. Flory–Huggins parameter

The solvent content dependence of the Flory–Huggins parameter is plotted in Fig. 2(a). For the d-PB(1,4)/PS blend, the enthalpic and entropic portions continuously increase with increasing solvent content. The d-PB(1,2;1,4)/PS blend yields an increase at low and high solvent contents and a decrease at intermediate solvent contents (2.5%–10%). We discuss this behavior in the free-volume section.

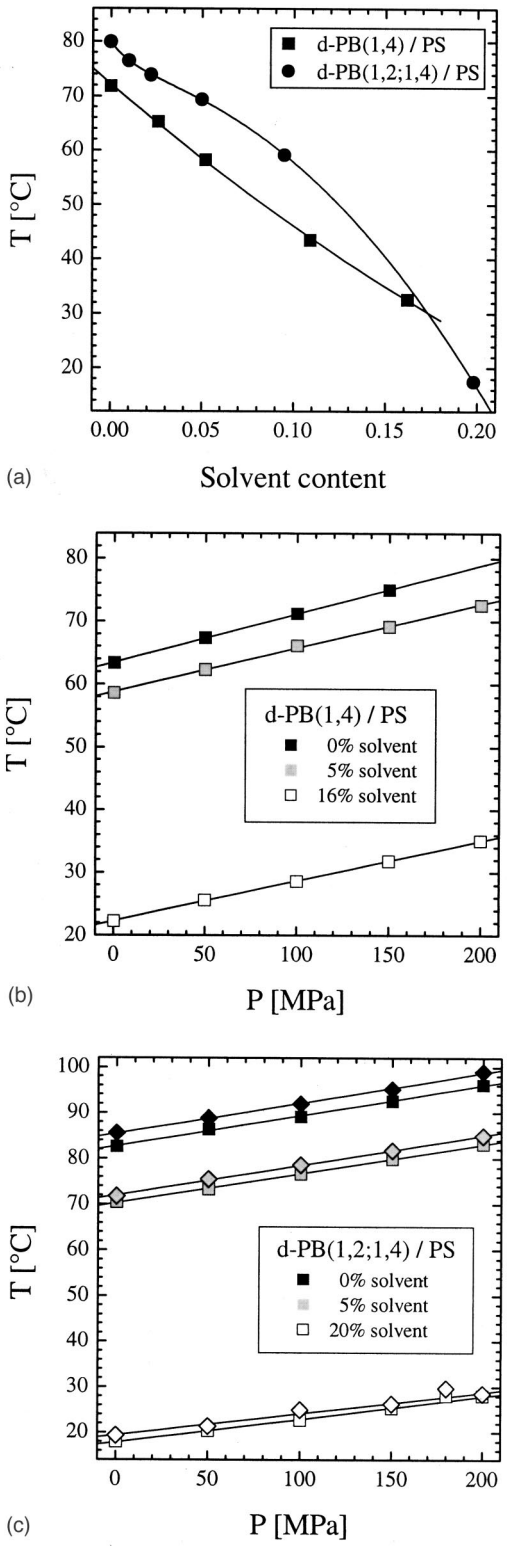

FIG. 1. The spinodal temperatures as a function of solvent content (a) for the two different PB microstructures. The spinodal temperatures as a function of pressure for the d-PB(1,4)/PS blend with different solvent contents (b), and for the d-PB(1,2;1,4)/PS blend with different solvent contents (c). The last figure also includes the binodal temperatures (♦), since here they were distinguishable within the figure resolution and otherwise they were not.

Figures 2(b) and 2(c) display the individual portions of the Flory–Huggins parameter as continuously decreasing with pressure for all solvent contents and both blends. The d-PB(1,4)/PS blend likewise yields a linear decrease without

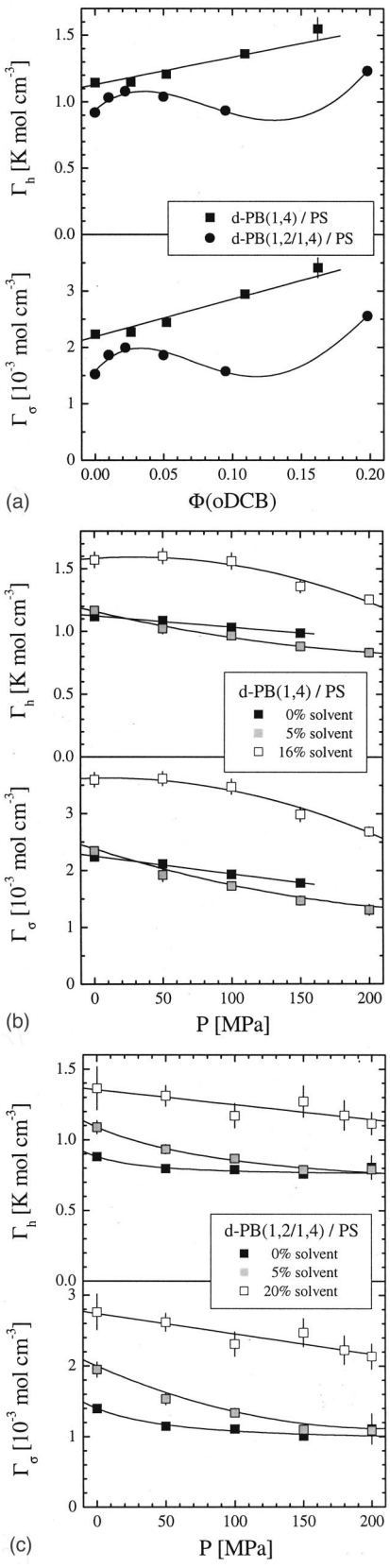

FIG. 2. The enthalpic and entropic portion of the Flory–Huggins parameter (Γ_h, Γ_σ) as a function of solvent content for the two different PB microstructures (a). The portions of the Flory–Huggins parameter as a function of pressure for the d-PB(1,4)/PS blend with different solvent contents (b), and for the d-PB(1,2;1,4)/PS blend with different solvent contents (c).

solvent addition. We find a stronger decrease upon the addition of 5% solvent: the 5% solvent line crosses the 0% solvent line at about 25 MPa. Thus, at high pressures the 5% solvent sample has lower entropic and enthalpic portions than the 0% sample. The 5% sample seems to saturate at 200 MPa. For 16% solvent content, the portions of the Flory–Huggins parameter are larger for all pressures. The 16% sample has a weak pressure dependence below 100 MPa, which becomes stronger above this pressure.

The d-PB(1,2;1,4)/PS Flory–Huggins parameter exhibits saturation for 0% and 5% solvent content at high pressures. The saturation values seem to be quite similar, but the 5% solvent values of the Flory–Huggins parameter are greater than or equal to the pure blend values for all pressures. The 20% magnitudes are even larger and show a linear pressure dependence.

C. Radius of gyration

The dependence of the radius of gyration on solvent content seems to be almost suppressed within experimental error [Fig. 3(a)]. The d-PB(1,4)/PS blend has a larger radius of gyration since the PB(1,4) chain is more elongated than the corresponding PB(1,2;1,4) polymer. The 15% difference between the PB and PS average radii of gyration is similar in magnitude to reports in the literature, where for pure PB a change of 10% was found.[21]

The pressure dependence of the radius of gyration generally seems to show a slight decrease, which almost vanishes within the accuracy of the data. Again, the 0% and 16% solvent content curves for the d-PB(1,4)/PS blend are almost indistinguishable. The 5% sample produces a surprising increase by about 11% from a solvent content-independent value at 0.1 MPa. In contrast, the radius of gyration of the d-PB(1,2;1,4)/PS blend shows a slight decrease with pressure for all solvent contents, i.e., within the experimental error the three curves agree.

D. Free volume

In this section we try to distinguish different contributions to the entropic portion of the Flory–Huggins parameter. Mainly, the free volume and the solvent content contributions can be extracted following Eq. (11). We assume that at the highest experimental pressure (200 MPa) the free-volume contribution to the entropic portion is practically vanishing. Then, the entropic contribution is described by a straight line, which is depicted in Fig. 4(a) with a slope equal to the reciprocal of the volume Ω_S associated with the solvent. The intercept is a residual entropic contribution Γ_σ^0 that arises from neglected features of the presently used theory, namely monomer structure, chain-end effects, and chain semiflexibility. This residual Γ_σ^0 is not decomposed further here as it would require the use of much more complicated LCT models.[3,7,8,10,17]

For the d-PB(1,4)/PS blend, we find the parameters $\Omega_S = 88\,\mathrm{cm}^3/\mathrm{mol}$, and $\Gamma_\sigma^0 = 0.73 \cdot 10^{-3}\,\mathrm{mol/cm}^3$, while the d-PB(1,2;1,4)/PS blend yields the parameters as $\Omega_S = 143\,\mathrm{cm}^3/\mathrm{mol}$, and $\Gamma_\sigma^0 = 0.74 \cdot 10^{-3}\,\mathrm{mol/cm}^3$. The values

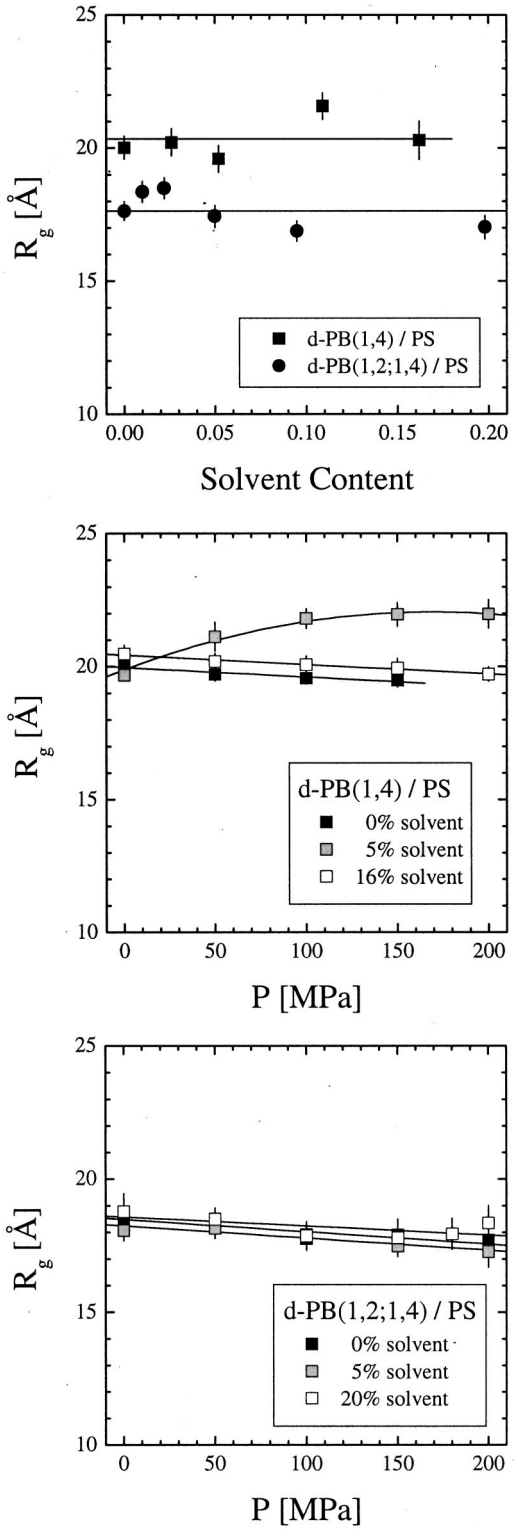

FIG. 3. The radius of gyration as a function of solvent content for the two different PB microstructures (a). The radius of gyration as a function of pressure for the d-PB(1,4)/PS blend with different solvent contents (b), and for the d-PB(1,2;1,4)/PS blend with different solvent contents (c).

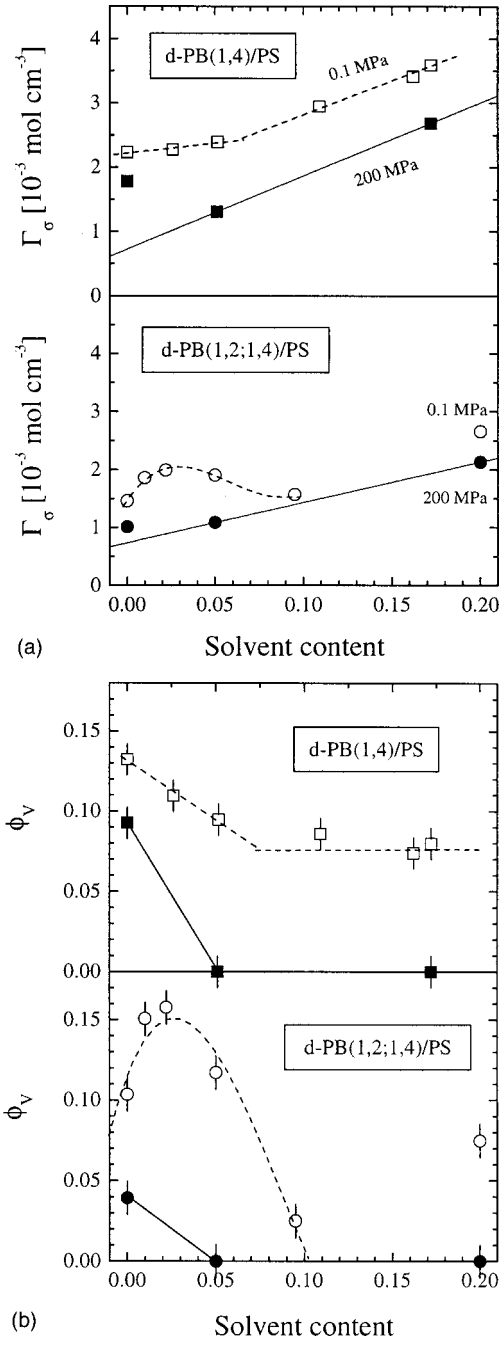

FIG. 4. The entropic portion of the Flory–Huggins parameter (a) as a function of solvent content for the pressures 0.1 and 200 MPa, and for the two PB microstructures. The solid lines are interpreted with Eq. (11) without any free volume. The dashed lines are guides for the eye. The resulting free volume (b) as a function of solvent content for pressures of 0.1 and 200 MPa, and for the two PB microstructures. The solid and dashed lines are guides for the eye corresponding to 200 and 0.1 MPa.

of Γ_σ^0 agree astonishingly well. A consideration based solely on monomer structures[6] would lead to values of around $\Gamma_\sigma^0 = -0.1 \cdot 10^{-3}\,\mathrm{mol/cm^3}$, while including chain semiflexibility[10] (with the bending energies of Ref. 8) would not change the general estimate. On the other hand, chain-end effects typically[11,6] lie in the range of $+1 \cdot 10^{-3}\,\mathrm{mol/cm^3}$ for this molar volume of $2 \cdot 10^3\,\mathrm{cm^3/mol}$ and, therefore, are probably dominant for Γ_σ^0. So, the common values for Γ_σ^0 seem to emerge from the similarity of the chain-end effects in the two blends.

The values for Ω_S basically agree with the volume obtained from the solvent density of 115 $\mathrm{cm^3/mol}$. In other words, when the solvent content is above 5% and the pressure is 200 MPa, the entropic part of the Flory–Huggins

parameter is just the purely combinatorial entropy, evaluated based on units equal to Ω_S. We find it plausible that the units of volume for the added solvent and the excess free volume are comparable [discussion of Eq. (11)]. Therefore, as an approximation we set Ω_V and Ω_S equal for each blend separately and interpret the differences in the $\Gamma_\sigma = \Gamma^0_\sigma + \phi_S/\Omega_S$ line as the contribution from the combinatorial entropy being proportional to ϕ_V/Ω_V. The results are presented in Fig. 4(b).

When solvent is absent and the pressure is 200 MPa, we find the fraction of excess free volume to lie in the range of 4%–9%. The vanishing of the free-volume content at 200 MPa must therefore appear somewhere between 0% and 5% solvent content. This means that solvent molecules occupy the regions associated with excess free volume in the pure melt, a phenomenon we term a "compensation of the free volume by the solvent." For the pressure of 0.1 MPa, we can draw a more detailed picture since more data points are available. The free-volume content for the d-PB(1,4)/PS blend decreases linearly from 13% to 8% at 8% solvent content and then stays constant at around 8%. Here, a compensation of the free volume occurs only partially. A slightly more complicated behavior is found for the d-PB(1,2;1,4)/PS blend where the free-volume content first increases with solvent content from 10% to 16% and then decreases to 2.5% at a solvent content of 9.5%. The high solvent content limit of the free-volume content again lies at around 8%. This increase in the excess free volume with the low molar mass additive indicates the creation of excess free volume due to a geometrical mismatch in a similar fashion as the production of the excess free volume associated with chain ends and side groups. We cannot explain why we find this *softening* effect for the d-PB(1,2;1,4)/PS blend and not for the d-PB(1,2;1,4)/PS blend. The further addition of solvent to the d-PB(1,2;1,4)/PS blend leads to a strong compensation of the free volume before the high solvent content value of 8% free volume is reached. In either case, the range of solvent contents, where the compensation of the free volume has reached its maximum, lies between 8%–10%.

E. Clausius–Clapeyron equation

The theoretical [from Eq. (14)] and experimental pressure dependence of the critical temperature agree quite well (Fig. 5). Whereas at low solvent concentrations the mean-field contribution dominates the pressure dependence of the spinodal, at higher solvent contents the Ginzburg number term for d-PB(1,2;1,4)/PS influences the pressure dependence strongly. A similar relationship is also found for the d-PB(1,4)/PS blend at 5% solvent content. When the solvent content reaches 16%, the influence of the Gi contribution is diminished. The derivatives are determined by polynomial fits to the experimental data points. The low influence of Gi in the 16% sample results from the derivative at 0.1 MPa, which becomes stronger at higher pressures in agreement with the other solvent-containing samples. We therefore stress that the Gi contribution generally becomes more important for higher solvent contents.

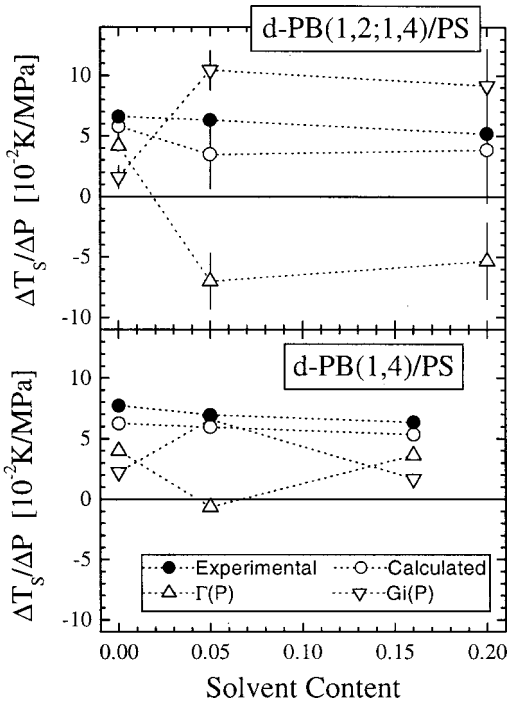

FIG. 5. The temperature/pressure gradient interpreted with different contributions of the Clausius–Clapeyron equation. The filled symbols (●) correspond to experimental values, and the open circles (○) to the ones calculated by Eq. (14). The latter ones are split into contributions from the Flory–Huggins parameter (△) and the Ginzburg number (▽).

IV. SUMMARY AND DISCUSSION

This paper presents experimental data and analyses of mean-field properties of homopolymer blends with the addition of solvent and over a range of temperatures and pressures. The blends studied consist of polybutadiene with either (1,4) or mixed (1,2;1,4) microstructures and polystyrene. The solvent is ortho-dichloro-benzene. The first paper (Part I) analyzes the susceptibility and the correlation length using a crossover function that describes the transition between 3D-Ising behavior near the critical point and mean-field behavior far from the critical point. This crossover data treatment yielded the mean-field critical amplitudes for the susceptibility and the correlation length in order to compare and interpret the data using mean-field theories. Using these mean-field quantities, we obtained the Flory–Huggins interaction parameter and the radius of gyration. Furthermore, we discuss the variation of the critical and binodal temperatures with the addition of solvent.

We found a complementary behavior of pressure and solvent. Whereas the addition of solvent enhances the miscibility of the two polymers, the miscibility decreases with increasing pressure. When discussing compressibility using an excess free-volume picture, it becomes clear that an applied pressure reduces the amount of free volume present, which is the opposite effect of requiring more space for the added solvent.

The entropic portion of the Flory–Huggins parameter increases with increasing solvent content. This experimental finding is amplified by the dilution approximation[19] in which Γ is formally replaced by $\Phi_P\Gamma$, with Φ_P being the total

polymer volume fraction. The observed strong dependence of the Ginzburg number[15] on Φ_P now arises due to three contributions: Φ_P itself, the entropic portion of the Flory–Huggins parameter which varies as $\Gamma_\sigma \propto \Phi_P^{-2.4}$ and $\Phi_P^{-1.6}$, and the critical amplitude which varies as $C_+ \propto \Phi_P^{-1.0}$ and $\Phi_P^{-2.2}$ for the PB(1,4)/PS and PB(1,2;1,4)/PS blends, respectively. The large exponent 4.2 in Eq. (8) of Ref. 15 finally explains the large exponents (≈ -10) observed for the Ginzburg number as a function of Φ_P. As in the pressure dependence of the Ginzburg number, where the entropic portion of the Flory–Huggins parameter plays a key role, we deduce that important contributions emerge from Γ_σ to the variation of the Ginzburg number with Φ_P.

A detailed discussion of the Flory–Huggins parameter showed a saturation effect at high pressures. We then discussed the entropic portion of the Flory–Huggins parameter Γ_σ at 200 MPa and its dependence on the solvent content and a residual entropy using the assumption that the free-volume contributions of Eq. (11) are absent at this highest pressure. The residual entropy Γ_σ^0 is mainly influenced by chain-end effects, because of the relatively low molecular weights for the polymers in these fairly immiscible blends, and disparities in monomer sizes and shapes. Using experimental data for the influence of added solvent at high pressures, we then determined the dependence of the Flory–Huggins parameter on the excess free volume for low pressures. Low and high pressures lead to a compensation of the free volume by the solvent. For the d-PB(1,2;1,4)/PS blend, an increase of the free volume at low solvent contents was interpreted as a softening process.

The dependence of the Flory–Huggins parameter on the solvent and free volume content is about 2000 times stronger than predicted by the lattice theory applied here. The reason for this discrepancy is the assumption that the polymers are quite similar (i.e., occupy the same lattice sites) and that neither void nor solvent is selective. Such simplifications result in Eq. (B2), with the small prefactor of $(1/N_1\text{-}1/N_2)^2$ describing a chain-end effect, and motivate the general form of the entropic portion of the Flory–Huggins parameter in Eq. (11). This simplified general form can only be applied to the actual system[22] with freely varying coefficients Ω_S and Ω_V. The structural differences between PB and PS can explain the much stronger dependence of the Flory–Huggins parameter,[7] but such an analysis requires the use of the full lattice cluster theory with the laborious need to determine six interaction energies, a procedure that is beyond the more qualitative approach pursued here. A possible selectivity of the free volume could be a further reason, and was already discussed in the context with the renormalized Ising behavior (Part I).

The application of the Clausius–Clapeyron equation provides a check on the use of the crossover function to extract mean-field quantities from experimental data. The measured and predicted [based on Eq. (14)] pressure dependence of the critical temperature agree well. It was found that either the Ginzburg number or the Flory–Huggins parameter terms dominate the pressure dependence of T_C under different conditions. At solvent contents above 5%, the influence of the Ginzburg number term is most important. This finding compares well with the d-PB(1,2)/PS system,[5] where a high vinyl side group content shows the same effect as solvent addition.

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APPENDIX A: EXPANSION OF THE SUSCEPTIBILITY

The starting point is the partial structure factor [Eq. (4)], which originally involves expressions in terms of $\partial n/\partial \mu$. Within our lattice model, all formulations are based on the thermodynamic potential F, where the natural variables are T, V, and n_i. Therefore, it is much easier to evaluate the matrix

$$\{m\}_{ij} = \left\{ \frac{\partial \mu}{\partial n} \right\}_{ij}, \tag{A1}$$

and invert it subsequently in order to obtain the desired matrix $\{\partial n/\partial \mu\}$. We finally project this matrix with a vector that selects contributions only arising from the polymer–polymer correlations, thereby obtaining the measurable susceptibility. In this way, we neglect correlations between the polymers and either the excess free volume or the solvent, which means that neither the excess free volume nor the solvent is selective to one of the polymers. Furthermore, the self-correlations of the free volume and the solvent are typically orders of magnitudes smaller than the polymer–polymer correlations. Within this approximation, the measured susceptibility is proportional to

$$\mathrm{proj}(m^{-1}) = \frac{1}{2}(1-10)m^{-1}\begin{pmatrix} 1 \\ -1 \\ 0 \end{pmatrix} = \frac{1}{2}\frac{(m_{AA}+m_{BB})m_{SS} - m_{AS}^2 - m_{BS}^2 + 2m_{AB}m_{SS} - 2m_{AS}m_{BS}}{m_{AA}m_{BB}m_{SS} + 2m_{AB}m_{BS}m_{AS} - m_{AA}m_{BS}^2 - m_{BB}m_{AS}^2 - m_{SS}m_{AB}^2}. \tag{A2}$$

This expression is still quite lengthy despite our use of symmetry properties of the matrix m. The following expansion is based upon the fact that individual matrix elements of m are dominated by a contribution from the translational entropy which is expressed in terms of the excess free volume, i.e., each matrix element contains a term $1/(\phi_V V_{\mathrm{cell}})$ which is about two orders of magnitude larger than the remaining contributions. Only m_{SS} contains a second large term $1/(\phi_S V_S)$ from the solvent. Thus, we can expand in the small asymmetry between the two polymers by writing

$m_{BB}=m_{AA}+\delta_{BB}$ and $m_{BS}=m_{AS}+\delta_{BS}$ and by expanding in powers of the δ. This expansion yields

$$\begin{aligned}\mathrm{proj}(m^{-1})^{-1}&=m_{AA}-m_{AB}+\delta_{BB}+O(\delta_{BB}^2,\delta_{BS}^2)\\&=\tfrac{1}{2}(m_{AA}+m_{BB})-m_{AB}+O(\delta_{BB}^2,\delta_{BS}^2).\end{aligned}\tag{A3}$$

This form of the projected matrix m is used here, while the next higher order term involving δ_{BB}^2 is

$$\begin{aligned}&-\frac{1}{2}\delta_{BB}^2\frac{m_{SS}}{(m_{AA}+m_{AB})m_{SS}-2m_{AS}^2}\\&\quad\approx-\frac{1}{4}\frac{1}{V_{\mathrm{Samp}}k_BT}\delta_{BB}^2\frac{\phi_V V_{\mathrm{cell}}+\phi_S V_S}{(\phi_A/n_A)^2}\\&\quad\approx-\frac{1}{4}V_{\mathrm{Samp}}k_BT(\phi_A/n_A)^2\left(\frac{1}{\phi_B V_B}-\frac{1}{\phi_A V_A}\right)^2\\&\qquad\times(\phi_V V_{\mathrm{cell}}+\phi_S V_S).\end{aligned}\tag{A4}$$

The approximation on the right-hand side arises only from the translational entropy and the solvent, terms for which the two polymers exert equivalent effects because of the use of a common lattice site for monomers, solvent molecules, and voids. Since the actual solvent is not polymer selective,[22] we do not discuss further higher order terms involving δ_{BS}. It should be mentioned that the projection of the matrix m also leads to these expressions. As a consistency check, we proved that the expansion of the dominant eigenvalue of $\{m\}$ shows the same behavior. Just small quantitative deviations were found for second-order terms. Combining (A3) and (A4), we arrive with the prefactors for Eq. (4)

$$\begin{aligned}\frac{1}{\Phi_P S(0)}&=\frac{1}{V_{\mathrm{Samp}}k_BT}\left(\frac{\partial^2 F}{\partial\phi_A^2}+\frac{\partial^2 F}{\partial\phi_B^2}-2\frac{\partial^2 F}{\partial\phi_A\partial\phi_B}\right)\\&\quad-\frac{1}{2}\left(\frac{1}{\phi_B V_B}-\frac{1}{\phi_A V_A}\right)^2(\phi_V V_{\mathrm{cell}}+\phi_S V_S).\end{aligned}\tag{A5}$$

The first term in Eq. (A5) describes the leading model-dependent contribution to the reciprocal susceptibility. The second term describes an entropic contribution to the Flory–Huggins parameter. For the d-PB(1,4)/PS blend, we evaluate the second term as $-2.2\cdot10^{-7}(\phi_V+\phi_S)\mathrm{mol/cm}^3$. This contribution is relatively small due to the difference of the $1/\phi_i V_i$ terms between the two components. In the following Appendix we find larger contributions.

APPENDIX B: CONTRIBUTIONS FROM THE INTERACTION PARAMETERS g_{ij}

The first term of Eq. (A5) is now evaluated with a more detailed model, which starts from Eq. (3). The lattice model of Bawendi and Freed[16] gives more details on the interaction parameters of Eq. (3). This simple model treats the polymers as simple linear polymers with one monomer occupying one lattice site. The solvent molecules occupy single lattice sites, and the excess free volume is described by allowing some lattice sites to be vacant

$$g_{ij}=f_{ij}^0+f_{ij}^1-s_{ij}.\tag{B1}$$

The interaction parameters g_{ij} are decomposed into three contributions. The zeroth-order mean-field energetic contributions are described by f_{ij}^0. The nonrandom mixing corrections to the energetic contributions are given by f_{ij}^1, and the entropic contributions by s_{ij}. Following the calculations of Bawendi and Freed[16] and Eqs. (8) and (9), we obtain the entropic portion of the Flory–Huggins parameter as

$$\begin{aligned}\Gamma_\sigma=&-\frac{2}{V_{\mathrm{cell}}z^2}\left(\frac{1}{N_A}-\frac{1}{N_B}\right)^2\Bigg(10+z+\left(-18+\frac{22}{N_A}\right)\phi_A\\&+\left(-18+\frac{22}{N_B}\right)\phi_B+12\Bigg(\left(1-\frac{1}{N_A}\right)\phi_A\\&+\left(1-\frac{1}{N_B}\right)\phi_B\Bigg)^2\Bigg).\end{aligned}\tag{B2}$$

For the PB(1,4)/PS blend, we use the following model parameters: $N_A=35$, $N_B=16$ are the degrees of polymerization, and $V_{\mathrm{cell}}=77\,\mathrm{cm}^3/\mathrm{mol}$ is the averaged monomer volume. Then, with these numbers we arrive at

$$\begin{aligned}\Gamma_\sigma=&-8.3\cdot10^{-7}\,\mathrm{cm}^{-3}\,\mathrm{mol}(9.9-5.2(\phi_V+\phi_S)\\&+11.3(\phi_V+\phi_S)^2+O(0.1)\phi_B+\cdots).\end{aligned}\tag{B3}$$

The overall coefficient of $(\phi_V+\phi_S)$ is now $4.3\cdot10^{-6}\,\mathrm{cm}^{-3}\,\mathrm{mol}$, which is 20 times larger than the comparable term in (A5). Nonetheless, this coefficient still leads to relatively small entropic contributions to the Flory–Huggins parameter. The reason is the factor $(1/N_1\text{-}1/N_2)^2$, which makes this contribution small similar to chain-end effects. The large structural differences between PS and PB similarly creates much larger terms,[7] which are neglected in this model. Nonetheless, here the entropic contributions are again proportional to $(\phi_V+\phi_S)$. These results motivate describing the leading contributions to entropy from excess free volume and solvent molecules with the form $\alpha(\phi_V+\phi_S)$. Furthermore, this also motivates the belief that the higher order contributions to Eq. (A5) are negligible, thereby supporting the form of Eq. (8).

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